

# Nano-Structure High Explosives using Sol-gel Chemistry

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98-ERD-048

**T**his project represents the first scientific inquiry using sol-gel chemistry in explosive synthesis. The use of sol-gel methodology offers the exciting possibility to control the microstructure of energetic materials on the nanometer scale, resulting in new or improved properties. The new micro- and meso-porous materials will also enable understanding initiation and detonation mechanisms, mass transport, and intramolecular reaction kinetics in the nanometer range.

Sol-gel chemistry produces high surface area, porous solids, which may be cast to near-net shape. The microstructure, comprised of nanometer-sized pores and linked primary particles, as well as the elemental composition, can be controlled by solution chemistry. In the general sol-gel process, monomers are reacted in a solution to produce 2–20 nanometer diameter primary particles, called “sols,” which can be linked to form a solid network surrounded by a liquid, called a “gel.” Controlled evaporation of the liquid phase results in a dense, porous solid, or “xerogel.” Highly porous, lightweight solids, “aerogels,” are produced by removing the liquid by supercritical extraction without collapsing the structure.

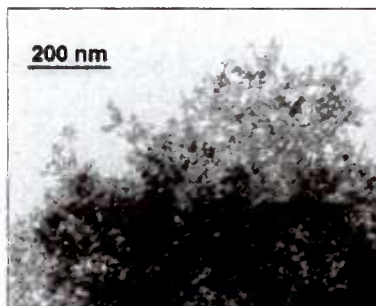
Several problems in energetic materials may be addressed by this methodology. One example is the fabrication of detonator materials where low manufacturing rates, difficulty in handling fine powders, and the inability to produce geometric shapes are current limitations. Using sol-gel chemistry, the intimacy of mixing can be controlled and dramatically improved over the state-of-the-art mixing of granular solids while providing a method for easily casting complex geometric shapes. Increased dimensional control will also enable high quality experiments to be run where chemical and mass transport limited kinetics may be determined more accurately than by conventional approaches. The next generation detonation models will focus on chemical kinetics and species equilibrium that rely on these data.

Numerous synthetic routes are possible utilizing this method in processing energetic materials. We have focused this work on four approaches: solution crystallization, powder addition, nano-composites, and functionalized/explosive solid networks. In FY98, we produced nano-structured high explosives by the first three approaches. Differential scanning calorimetry (DSC) confirmed the presence of the energetic materials in the final dried products. Monolithic aerogels were prepared by the solution crystallization of hexahydro-1,3,5-triazine (RDX). Monolithicity was maintained up to 45 wt% RDX in a 55% SiO<sub>2</sub> matrix. In the lowest composition, 17 wt% RDX, the crystals are not visible to the naked eye, while increasing compositions result in micron-sized

orthorhombic crystals. Using the powder addition approach, high solids loading was accomplished and reported for the first time by a gel-mending method. The impact sensitivity of an energetic material to unintended initiation is an important safety factor in its use. Counter to expectations, drop hammer sensitivity tests showed that the presence of the gel structure decreased the impact sensitivity of an explosive. De-sensitized materials are only an improvement in technology if they can still be initiated with reasonable power outputs. A flyer-plate experiment demonstrated that possibility when an 80% RDX xerogel moulding powder pressed into a detonator pellet could be initiated. Remarkably, we found that RDX in silica-based xerogels failed to initiate when shocked at pressures adequate to initiate TATB.

A prototype nano-composite (see figure) was made by crystallizing ammonium perchlorate (AP) within the pores of an organic gel. In this composite, the solid hydrocarbon skeleton comprises the fuel with the AP acting as the oxidizer. Compositions with the energy density of HMX have been made. Transmission electron microscopy (TEM) indicated no crystallites greater than 20 nm. Near-edge soft X-ray spectroscopy performed at LBNL's Center for Microscopy showed that nitrogen was uniformly distributed to the resolution limit of 80 nm. With this technology readily scaleable to large quantities, a material goal—that has eluded conventional technology—to create a material that has the energy of strategic rocket propellant with the power of an ideal explosive may be possible.

In FY98, collaboration with the Navy resulted in nano-composites where aluminum, a fuel, was crystallized within skeletal structures using in-situ chemical processes. Other accomplishments include synthesizing aerogel gas generators by polymerizing 1,3 diaminobenzene, and developing a non-aqueous based organic aerogel route, which significantly reduces processing time. In FY99, we will continue to develop new sol-gel synthetic routes, emphasizing characterization of the new energetic materials.



Ammonium perchlorate/resorcinol-formaldehyde (AP-RF) nano-composite made by crystallizing ammonium perchlorate within the pores of an organic gel. Resorcinol-formaldehyde is the classic polycondensation reaction for making organic nano-structures.